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(54) IMPROVEMENTS IN POLYURETHANE SPONGES

(71) We, ROBERT L. STRICKMAN and MELVYN B. STRICKMAN, residing at 729 Handweg Drive, River Vale, New Jersey 07675 and Academy Street, Shiloh, New Jersey 08353 respectively, and both citizens of the United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to resilient polyurethane sponges and to methods of manufacturing them. Such sponges may be used for human bathing, animal bathing, washing dishes, scouring pots and pans, washing automobiles and various similar functions.

In general terms the polyurethane synthetic sponge skeletons with which the invention is concerned come within known urethane foam manufacture. The foam structures are developed by interaction of polyethers or polyesters with isocyanates.

According to this invention, a dry synthetic resilient polyurethane sponge has closed cells within which is a soap and/or a detergent, the soap and/or detergent forming at least 4% by weight of the sponge. A silicone oil, desirably in a non-pasty form, may be present with the soap and/or detergent in the sponge e.g. in an amount of 4 to 20% by weight of the sponge.

Sponges with silicone oils dispersed therein are especially suitable for cleaning and/or polishing automobile bodies and the like. Soaps and detergents are useful additives in sponges used for bathing and lotions, lanolin and bath oils may also be included in these. Pesticides are useful in sponges for bathing of pets. The sponges in accordance with the invention constitute inexpensive carriers for various additives as well as excellent applicators thereof.

An indication of the problems involved in incorporating additives of the types mentioned above in amounts of 4% by weight or more

in synthetic polyurethane sponges can be obtained by considering silicone oils, which are typical of these additives. It is known that silicone oils are foam depressants, as are others of the additives mentioned. Silicone oils and other surface active agents reduce surface tension of foaming systems, resulting in foams having small and uniform cells. Because of their surface activity, silicone oils delay foam collapse by decreasing initial bubble size and by delaying breaking of large bubbles. In polyurethane foams the cell size decreases with increasing concentration of silicone oils until it reaches a concentration, usually of about 1 part per 100 parts of prepolymer, when foam collapse occurs. Foam collapse occurs at additive concentrations of approximately the same order for the other additives mentioned. By way of example, in foam stabilising, the preferred range of dimethylsilicone oils is usually between 0.3 and 0.7 parts per 100 parts prepolymer. Very low viscosity (10, 50 and 100 centistokes) dimethylsilicone oils are widely employed, with the 50 centistoke oil being used most frequently. As viscosity of the silicone oils decreases, the silicone oils' requirement decreases, but the usable range of silicone oils' concentration become narrower. Such use of silicone oils is for the purpose of obtaining uniform cell structure. Concentrations of silicone oils and/or other reactive additives of the order of 10 to 25 times those used heretofore for foam stabilising may, in accordance with this invention, be dispersed in a sponge. These and higher concentrations of the additives may be used even though the additives are generally regarded to be active ingredients in the foam forming mechanism.

A sponge according to the invention may be made by a method comprising mixing a dry carrier, comprising a soap and/or a solid detergent, containing silicone oil distributed therein, with a fluid mass capable of foaming to form a polyurethane foam and allowing the mixture to form a resilient poly-

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urethane foam having closed cells within which is the carrier and silicone oil. In this way, the composition undergoing foam formation is insulated from foam depressing effects of the additives. We have discovered that when silicone oil (for example) is incorporated in a carrier, the combination of the carrier with the silicone oil can be included in the reaction mass undergoing foam formation, without impairment of the foam formation. This led us to the manufacture of sponges containing high contents of certain additives by preliminarily preparing an additive bearing material, i.e. a carrier containing the additive and then mixing the carrier into the foam forming reaction mass. In those sponges according to the invention which contain a silicone oil with the soap and/or detergent, it is preferred that the silicone oil should be incorporated in a carrier, preferably a soap. By means of the method sponges may be made containing, for example, 4 to 50% by weight of a silicone oil.

Sponges in accordance with the invention have a supporting sponge skeleton having a cell structure including closed cells although some open cells may also be present. The soap and/or detergent together with any other additive is trapped in individual closed cells and becomes available during the course of the use of the sponges because of rupturing of cells in mechanical handling of the sponges. Such physical disposition of additives allows for slow release thereof; and accordingly, provides for availability of the entrapped additives throughout the life of the sponge.

We further discovered that it is possible to incorporate a large quantity of abrasive scouring particles in a fluid mixture of synthetic foam ingredients and yet to effect rapid rise, gelation and cure thereof to assure uniformity of dispersion of the abrasive in the finished sponges. Accordingly, in a preferred type of sponge in accordance with the invention, abrasive scouring particles are present with the soap and/or detergent and the weight ratio of the particles to the polyurethane of the sponge is preferably from 4 to 6:1. Such sponges may be made by mixing a soap and/or a detergent and a hot mass of abrasive scouring particles with a material capable of foaming to form a polyurethane foam and allowing the mixture to expand freely and to cure to form a resilient polyurethane foam having closed cells within which is the soap and/or detergent and scouring particles.

The abrasive scouring particles at the time of incorporation thereof in the synthetic foam forming ingredients should preferably be so hot that the heat of the particles is transferred to the foam forming ingredients, thereby accelerating gelation and curing so that formation of the foam skeleton is completed within 3 to 5 minutes. Desirably, the particles have a temperature of from 65 to 125°C.

The sponges can have a particle-to-resin weight ratio of the order of 5—6 parts by weight of the particles to 1 part by weight of the polyurethane.

We have also found that, in manufacturing synthetic polyurethane sponges having high abrasive particle contents, besides using the well known catalysts customarily employed in catalysing the interaction of the polyethers or the polyesters with the diisocyanates, we can use alginates, for example, alkali metal or ammonium salts of alginic acid. These alginates are surprisingly not only excellent catalysts, but also aid in keeping the particles uniformly dispersed in the fluid reacting mass during the rising and gelation of the resin mixture undergoing polymerisation.

In the methods in accordance with the invention the foam forming material is preferably the reaction product of an aryl diisocyanate e.g. tolylene diisocyanate and a polyether e.g. polypropylene glycol.

Examples of types of sponges in accordance with the invention are as follows:—

A household soap product having a detergent and/or a soap-to-polyurethane weight ratio of about 4:1.

A car wash product having a synthetic detergent-to-polyurethane ratio of about 4:1.

A floor cleaning product, based on a combination of soap, synthetic detergent and abrasive, whereof the solids-to-polyurethane weight ratio is about 4—5:1, the soap-to-synthetic detergent-to-abrasive weight ratio of said solids being of the order of 1.25:1.15:3.5.

An upholstery cleaner having a high foaming synthetic detergent-to-polyurethane weight ratio of about 4:1.

A metal cleaning product containing synthetic detergent, soap and abrasive, whereof the total solids-to-polyurethane ratio is 5:1, the abrasive portion of said solids being from 2 to 3 times that of the synthetic detergent plus the soap, these latter two being used in approximately equal proportions.

Industrial cleaning products, for example, for use in cleaning aluminium sheets, whereof the abrasive content is fine mesh silica and/or alumina powder, in combination with a synthetic detergent and soap. The total solids-to-polyurethane ratio of this product is about 4—5:1, the fine mesh abrasive constituting about 75% of the solids; and the synthetic detergent and the soap being present in approximately equal proportions.

Another industrial cleaner is one in which there are used in place of the oxide abrasives described in the foregoing, any one or a mixture of comminuted metals, such as

metal filings of copper, aluminium or stainless steel.

It will be apparent that the skeletal structure of the sponge will provide for a variation in degree of resiliency, depending upon the selection of the specific materials used to provide the resinous skeleton. This selection is readily attainable in consequence of the known characteristics of foam or foam forming substances. Furthermore, these sponges can be provided with a variety of abrasives of various graded particle sizes and graded hardnesses. The selection of the abrasive components to provide desired abrading or polishing effect can readily be determined by preliminary testing based on the known qualities of the abrasives.

We have further found that when soap flakes and detergents (compatible with soaps) are both used as additives, it is advantageous to coat the granules of the synthetic detergents with soap, thus allowing for slower release of the detergent particles when the sponges are moistened.

Additives can be blended in a sponge in accordance with this invention by making up a separate sponge each with one or more of the additives therein. Then the separate sponges are shredded and portions thereof are blended into a foam forming reaction mass prior to foam formation whereby a new sponge with desired proportions of additives is made.

Micro-encapsulation can be employed to introduce large amounts of oils or other additives into sponges. Micro-encapsulated oil ingredients are mixed into the foam forming reaction mass prior to foam formation. It is also feasible to introduce oils by means of an oil absorbing substance which substance can then be added to the foam forming reaction mass before foam formation.

In cases where additives such as silicone oils are to be incorporated, it is clearly preferable to prepare preliminarily a carrier containing the additive, which carrier is then mixed into the reaction mass before foam formation begins, but it is possible also to proceed directly to the manufacture of the sponges from a prepolymer and suitable additives, a so-called "one shot" approach.

The following are Examples in accordance with this invention apart from Example 16 which illustrates a microencapsulation technique which may be applied to additives to be incorporated into sponges in accordance with the invention. In the Examples all parts, percentages and ratios are by weight.

Example 1

Step I Preparation of silicone-containing material

To a mass of 5 pounds of coco-tallow soap (low titer) in the form of large flakes, 2 pounds of dimethyl silicone (viscosity 350 CPS) are

added and gently incorporated, by letting the silicone flow onto the top of the mass of the soap flakes and allowing the mixture to stand for 5 minutes. The mass is then mixed in such a way as to avoid substantial breaking of the flakes. To this mass, 12 additional pounds of the aforesaid soap flakes were then added. The whole mass was handled to effect a thorough distribution of the silicone-coated soap flakes throughout it. 10 pounds of a linear alkylaryl sulfonate detergent, in the form of strong beads, were then added and the entire mass gently and thoroughly mixed to form a dry material containing the silicone.

Step II Preparation of the foam former

A. 100 weight parts of polypropylene glycol (molecular weight 2,000, hydroxyl No. 56) were introduced into a reactor in an inert atmosphere. To the glycol were added 9.1 weight parts of tolylene diisocyanate. The mixture was rapidly agitated and the temperature raised to and maintained for 3 hours at 120°C until the viscosity reached 15,000 CPS (Brookfield method, 25°C). There was then gradually added during 1 hour at 120°C, 24.5 weight parts of additional tolylene diisocyanate. This fluid was then brought to room temperature (about 20—25°C). The product is a prepolymer.

B. To 570 grams of the prepolymer produced in part A, there were added 35 grams of the following catalyst mixture:

1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	1.0 part
Triethanol amine	0.5 part
Water	1.9 parts
50% aqueous emulsion of dimethyl silicone	1.0 parts

The catalyst was mixed into the prepolymer and the mass stirred until foam formation was initiated.

Step III Incorporation of mixture produced in Step I with foam former

When the mass produced in Step II began to undergo foam formation, there were added 300 grams of the silicone-bearing material produced in Step I. The mass was thoroughly but gently mixed to avoid substantial fracturing and disintegration of the solid components of the mixture produced in Step I. The mixture was poured onto an open mold. The mass is allowed to rise, gel and set. On cooling, the solid resilient mass was cut into blocks of convenient size to form a synthetic sponge product of this invention.

Part A of Step II, as mentioned, is directed to the formation of the prepolymer. Instead of preparing the prepolymer, commercially available prepolymers, such as for example,

Resin F 202 (Nopco Chemical Co.), may be used for the manufacture of the foam former.

Example 2

A synthetic sponge was manufactured in accordance with the general procedure described in Example 1, with the inclusion, however, of ethylene diamine tetraacetic acid, which functions as a rust inhibitor. In this procedure, the silicone was embodied with the soap flakes as described in Step I of Example 1. To the soap flakes containing the silicone (total mass of 17 pounds) there was added about 1/2 ounce of sodium salt of ethylene diamine tetraacetic acid (versene beads) which was thoroughly mixed into the material, care being taken to avoid breaking the soap flakes. The alkylaryl sulfonate was combined therewith as in Step I of Example 1.

Example 3

A sponge was manufactured in accordance with the general method described in Example 1, but containing, in addition to the recited components, a small amount of a suitable ultraviolet light absorber, for example, 2,4-dihydroxy benzophenone. 15 grams of the ultraviolet light absorber were added at the stage in Step I just prior to the incorporation of the alkylaryl sulfonate beads. The compounded foam provides protection against degradation by sunlight, if used, for example, in automobile washing.

Example 4

A sponge was made in accordance with the general procedure described in Example 1 with the inclusion, however, of both the aforesaid ultraviolet light absorber and the ethylene diamine tetraacetic acid.

The silicone sponge products made in accordance with this invention can have a silicone content as high as about 10 to 20% of the mass. Suitable results, especially in cleaning automobile bodies and the like, are attained when the silicone content of the sponge is about 4.5%.

Example 5

To 1 pound of a 200 mesh cellulose flour were added 2 pounds of dimethyl silicone. After the silicone had been thoroughly absorbed, 27 pounds of a linear biodegradable alkylaryl sulfonate were added. This was thoroughly blended and mixed. The subsequent steps were the same as described in Example 1.

In the following examples, the general procedure of manufacture was that set forth in the foregoing examples. Accordingly, only the component materials and the amounts thereof in parts by weight are specified.

Example 6

Prepolymer	560	60
Silicone-vehicle-silicone combination:		
Coco-tallow soap	170	
Alkylaryl sulfonate	100	
Dimethyl silicone	27	65
Catalyst system:		
Triethanolamine	4	
1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	8	70
50% aqueous dimethyl silicone emulsion	8	
Water	8	

Example 7

Prepolymer	560	75
Silicone-vehicle-silicone combination:		
Coco-tallow soap	150	
Alkylaryl sulfonate	120	
Dimethyl silicone	32.4	80
Catalyst system:		
N-methyl-morpholine	4	
Triethanolamine	2	
1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	4	85
Diethanolamine	2	
50% aqueous dimethyl silicone emulsion	8	
Water	8	90

Example 8

Prepolymer	560	
Silicone-vehicle-silicone combination:		
Coco-tallow soap	160	95
Alkylaryl sulfonate	110	
Dimethyl silicone	25	
Catalyst system:		
N-methyl-morpholine	2	
Triethylamine	1	100
Triethanolamine	3	
1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	6	
50% aqueous dimethyl silicone emulsion	8	105
Water	8	
Rust preventive:		
Sodium salt of ethylenediamine tetraacetic acid	4	110
Ultraviolet light absorber:		
2 - hydroxy - 4 - methoxy - benzophenone	1	

Example 9

Prepolymer	560	115
Silicone-vehicle-silicone combination:		
Coco-tallow soap	140	
Alkylaryl sulfonate	130	
Dimethyl silicone	25	120

	Catalyst system:		going examples and the proportioning thereof may be varied. The choice of the component materials to be used and suitable proportioning thereof are determined easily by laboratory tests. The materials and the amounts thereof set forth in the various examples are those which we have found to be readily available and which give very suitable results. For instance, the alkylaryl sulfonate mentioned in the examples is the sodium salt of dodecyl benzene sulfonate. It is among the most widely used of the syndets. It is marketed by many of the largest manufacturers under well known trademarks, and is also available as an amine salt. However, other surfactants, particularly those which are biodegradable are also useful, including linear alcohol sulfates, sulfated fatty acids, amides, and esters, glycol esters, fatty alkanolamides, ethoxylated alcohols and phenols.	
	Triethanolamine	4		
5	1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	5		65
	N,N,N',N' - tetramethyl - 1,3 - butadiamine	3		
	50% aqueous dimethyl silicone emulsion	9		70
10	Water	7		
	Rust preventive:			
	Sodium salt of ethylene-diamine tetraacetic acid	3		
	Ultraviolet light absorber:			
15	Benzotriazone compound (as for example, Tinuvin P) ("Tinuvin" is a Trade Mark)	1		75
	Example 10			
20	Prepolymer	560	The sponges made in accordance with the foregoing examples are useful in consequence of their high silicone content, for cleaning of automobile bodies and for many other cleaning purposes. When used in cleaning panes of glass, the effect thereof is to prevent misting or steaming thereof. When applied, for example, to windshields the effect is very substantially to reduce fogging, or accumulation of water while driving through rain. A similar effect is observed in ski goggles and bathroom mirrors.	
	Silicone-vehicle-silicone combination:			85
	Coco-tallow soap	120		
	Alkylaryl sulfonate	150		
25	Dimethyl silicone	25		
	Catalyst system:			
	Triethanolamine	4		
	1,4 - bis - (2 - hydroxypropyl) - 2 - methylpiperazine	5		90
30	Octadecyl dimethylamine	3		
	50% aqueous dimethyl silicone emulsion	8		
	Water	8		95
35	Example 11			
	Example 1 was repeated except that the following was used as the catalyst in an amount of 3 parts per 100 parts of the prepolymer:			100
		parts		
40	Triethanolamine	80		
	Water	160		
	Triethylenediamine	12		105
	Silicone Surfactant (L 530 of Union Carbide or Dow Corning 100, etc.)	40		
45	Dibutyl Tin Laurate	0.2		
	Quadrol (Wyandotte Chemical Co.) n,n,n',n' - Tetrakis (2 hydroxypropyl) ethylenediamine	15		110
50				115
	A marked advantage of the synthetic sponges made in accordance with the foregoing examples is that during cleaning of an automobile body or the like, it does not remove wax coatings deposited thereon, as by Simonizing or porcelainizing. A further advantage of the sponges is that when they are immersed in water, the aqueous solutions thus produced have substantially neutral pH values.			
55	The selection of the component materials constituting the novel products of the foregoing			
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	Example 12			
	A Resilient Abrasive Sponge Product			
	Preparation of the abrasive content			
	A mass of abrasive particles, as for example, silica (mesh size 40-60), was heated until the temperature thereof is about 65-75°C.			120
	Preparation of the foam former			
	100 weight parts of polypropylene glycol			

(molecular weight about 2,000, hydroxyl No. 56) were introduced into a reactor in an inert atmosphere, as for example, nitrogen. To the glycol there were added 9.1 weight parts of tolylene diisocyanate. The mixture was rapidly agitated and the temperature raised to and maintained for 3 hours at 120°C until the viscosity reached 15,000 CPS (Brookfield method 25°C). There was then gradually added during 1 hour at 120°C, 24.5 weight parts of additional tolylene diisocyanate. This fluid was brought to room temperature (about 20–25°C).

To 100 weight parts of this fluid was added a mixture of 2.3 weight parts of water and 2.0 weight parts of N-methyl morpholine; and the mass was stirred for 5 seconds.

Mixing of the abrasive with the foam former 500 parts by weight of the hot abrasive particles (having a temperature as above) were mixed with 100 weight parts of the foam former (prepared as above), and the whole mass was vigorously stirred for about 50–60 seconds to assure uniformity of distribution of the resin in the viscous mass. A coconut oil soap was additionally incorporated to give a weight ratio of abrasive to soap of 350:70. The viscous mass was poured into a suitable mold (open cavity). The mass rose, gelled and cured in about 3 to 8 minutes.

On cooling, the solid resilient mass was cut into pads or blocks of convenient size to form scouring pads or blocks.

For the continuous manufacturing of the product, a stream of the hot abrasive particles, a stream of the foam former, and a stream of the catalyst were proportioned to feed simultaneously into a high speed mixing head provided with a continuous discharge. The discharged mixture was fed continuously into suitable molds.

The products can be suitably colored or tinted by including a suitable pigment or tinctorial agent in any of the ingredients.

Example 13

In accordance with the general procedure described in Example 12, a product was prepared in which in lieu of soap alone as the cleaning agent, there was employed a synthetic detergent with soap. The detergent and the soap were mixed preliminarily, as by tumbling, to effect a coating of synthetic detergent particles. The detergent particles employed can be the sodium alkyl sulfates, e.g., sodium ceryl sulfate, or sodium alkylaryl sulfonates, or the sodium salts of sulfonic acid derivatives of dialkyl dicarboxylates in the following approximate proportions: sodium alkyl sulfate, 40 parts; soap, 180 parts.

There may also be included therewith about 10 parts of carboxymethyl cellulose.

Example 14

Products were prepared in accordance with the general procedure described in Examples 12 and 13 except that in place of the mixture of the water and the N-methyl morpholine, there was used as the catalyst a 3% solution of sodium alginate in water.

Example 15

A product was made in accordance with the general procedure described in Example 12 using either the catalyst mentioned therein or that mentioned in Example 14 and, in lieu of the oxide abrasive particles, there was employed a mass of comminuted metal, such as iron, stainless steel, aluminium, copper or brass.

Although the skeleton-former described in the foregoing Examples 12–15 is currently preferred, other foam or sponge-forming resinous materials well known in the art can be used. The important feature is the high temperature of the abrasive particles when mixed with the foam former. The heat of those particles makes it possible to achieve and maintain uniform distribution of the large mass of the abrasive particles throughout the mixture thereof with the comparatively small amount of the foam former; and to accomplish the rapid rise, gelation and cure of the mixture.

It will also be understood that the cellular structure of the final abrasive product can be varied from sponge to foam character, including intermediate combinations thereof, depending upon the use of an open mold or a closed mold, with, in the case of the latter, control of the pressure.

Example 16

Microencapsulation

Step I Microcapsules of oils or silicone components were prepared as follows: 1100 grams of gelatin were dissolved in 1.8 liters of water, the water temperature being brought to not more than 54° to 55°C. 1000 grams of gum arabic were dissolved in 1.8 liters of water under the same condition.

Step II The warm solutions from Step I were mixed in a suitable container and heated to exactly 55°C. The solution was stirred and the pH value adjusted to 4.65 by addition of either 0.1 N NaOH or 0.1 N HCl.

Step III Oil fractions were added as follows: 9 kilos of isopropyl palmitate were added to the mixture with vigorous stirring, the mixture cooled slowly with stirring and the mixing continued until the temperature reached 10°C.

Step IV The microcapsules were separated from the aqueous solution and dried. The microcapsules were dried by treatment with suitable solvents. The size distribution of the microcapsules is determined by speed of stir-

ring, by the amount of oil and by micro-capsules wall components.

In the following examples, the general procedure of foam manufacture is according to the so called "one shot" system.

Example 17

	Pluracol Polyol G P 3030	100 gms.
	Hydroxyl Number 56	
	(Wyandotte Chemical Co.)	
10	Catalyst system per Example 11	2.6 gms.
	Tolylene diisocyanate (TDI)	
	80/20 mixture of 2, 4/2, 6 isomers	37.8 gms.

15 The catalyst was added to the polyol and blended. The TDI was then added. The mixture was stirred rapidly until it begins to cream. At this stage 30 gms. of a mixture consisting of 60% coco tallow soap and 40% of biodegradable linear alkyl aryl sulfonate (such as Sulframin 85 of Witco Chemical Co.) was added. The stirring was continued until the soap mix was uniformly dispersed. The mix was then poured into a suitable mold and left to foam.

Example 18

	Pluracol TP 4040 Polyol	70 gms.
	(Wyandotte Chemical Co.)	
	Pluracol TPE Polyol	
30	(Wyandotte Chemical Co.)	30 gms.
	Catalyst (same as in Example 17)	2.6 gms.
	Tolylene diisocyanate	35.6 gms.

35 17. The procedure was the same as for Example 17.

Example 19

	Foaming bath sponge	
	Olefin Sulfate (Sulframin of Witco Chemical Co.)	250 gms.
40	Coco Tallow Soap	50 gms.
	Hypoallergenic Lanolin Derivative (Solulan 95 of Amerchol Chemical Co.)	10 gms.

45 The Solulan 95 was added to the soap flakes and mixed with the Olefin Sulfate. The subsequent procedure was similar to that in Example 1, using the following amounts of prepolymer and catalyst.

50	Prepolymer	100 gms.
	Catalyst	3 gms.

Example 20

	Soap-Detergent Mix	
	As in Example 19	40 gms.

55 The prepolymer and catalyst blend were mixed until creaming was uniform. The soap

mix was then added with stirring until it was uniformly dispersed. The mixture was then poured into suitable molds.

The procedure of this example can also yield a sponge for a pet (dog or cat or the like) by addition of a suitable pesticide.

Example 21

Detergent sponge with scrubber top
To a sponge sheet prepared in accordance with Example 17, the following was knife coated or roller coated on Teflon rolls ("Teflon" is a Trade Mark).

	Prepolymer	100 gms.
	Catalyst	2.5 gms.
	Dow Corning 100 Silicone	2.0 gms.

The above components were thoroughly mixed until uniform creaming was observed. The following formulation was added and then stirred until foaming began. After the foam rose, it collapsed and bubbled. At this stage a very thin layer was coated on the sponge sheet. This can be done on a batch or a continuous bases. A hard flexible scrubbing surface was formed on the sponge sheet.

	*Lipo Foam (Lipo Chemical Corp.)	24 gms.
	Emcco L CDA	2.5 gms.
	Water	25 gms.

*Use 5 gms. per 100 gms. of prepolymer.

Example 22

	Detergent abrasive sponge (iron rust)	
	Prepolymer	100 gms.
	Catalyst	3 gms.

The above components were mixed until the mixture began to cream. The following was then rapidly added:

	30 gms. of Soap Mix	
	150 gms. of Abrasive or Aluminium Oxide	95

The resultant composition was mixed at high speed until the mixture was uniform. The mixture was then poured into suitable molds.

	Soap Mix:	100
	60% Coco Tallow Soap in flakes or granules	
	40% Linear Alkyl Aryl sulfonate (Biodegradable)	

	Abrasive Mix:	105
	Stainless Steel 60—80 Mesh 80%	
	Stainless Steel 240 Mesh 20%	
	Aluminium Oxide:	
	60—80 Mesh 100%	

Example 23

Detergent abrasive sponge

Soap Mix:

- 5 Coco tallow soap 60%
 Linear alkyl aryl sulfonate 40%
 30—40 gms. per 100 gms. of prepolymer
 40—60 gms. to 100 gms. of polyol

Abrasive:

- 10 Stainless Steel 80 mesh 80 gms.
 Stainless Steel 240 mesh 20 gms.

The procedure was similar to that in Example 22.

Example 24

Detergent abrasive sponge

- 15 Coco tallow soap 60%
 Linear alkyl aryl sulfonate 40%

Abrasive Mix: 80—100 mesh Al_2O_3

The procedure was similar to that in Example 23.

Example 25

Bubble shower bath sponge

- 20 Solulan C-24. Ethoxylated
 lanolin derivative (Amer-
 chol Chemical Co.) 5%
 25 Hexylene Glycol. Alkyl-
 amide of coconut fatty
 acid and diethanolamine 10%
 Monamide 150 AD
 (Mona Industries, Inc.) 20%
 30 Triethanolamine lauryl sul-
 fate 65%

- 35 The Solulan C-24 was melted by warming
 and mixed thoroughly with the other com-
 ponents. The mixture was absorbed on about
 15 gms. of Strickite oil collector per U.S.
 Patent 3,657,125 until the appearance was
 that of a solid gel.

Prepolymer 100
 Catalyst 3

- 40 The prepolymer and catalyst were mixed
 until uniformly creamed. The mixture
 absorbed on the Strickite was then added to
 the prepolymer/catalyst mixture with rapid
 stirring and the resultant composition poured
 45 into moulds.

WHAT WE CLAIM IS:—

- 50 1. A dry synthetic resilient polyurethane
 sponge having closed cells within which is a
 soap and/or a detergent, the soap and/or
 detergent forming at least 4% by weight of
 the sponge.
 2. A sponge according to claim 1 in which
 abrasive scouring particles are present with
 the soap and/or detergent.

3. A sponge according to claim 2 in which
 the weight ratio of the abrasive particles to
 the polyurethane of the sponge is from 4 to
 6:1.

4. A sponge according to any preceding
 claim in which a silicone oil in non-pasty
 form is present with the soap-and/or deter-
 gent.

5. A sponge according to claim 4 in which
 the silicone oil forms 4 to 20% by weight
 of the sponge.

6. A sponge according to any of claims 1
 to 3 in which a silicone oil, incorporated in
 a carrier, is present with the soap and or
 detergent.

7. A sponge according to claim 6 in which
 the carrier is a soap.

8. A sponge according to claim 1 substan-
 tially as hereinbefore described with reference
 to any of the Examples.

9. A method of making a sponge accord-
 ing to claim 1 comprising mixing a dry carrier,
 comprising a soap and/or a solid detergent,
 containing silicone oil distributed therein,
 with a fluid mass capable of foaming to form
 a polyurethane foam and allowing the mix-
 ture to form a resilient polyurethane foam
 having closed cells within which is the carrier
 and silicone oil.

10. A method according to claim 9 in which
 the silicone oil content of the sponge pro-
 duced is from 4 to 50% by weight.

11. A method according to claim 9 or claim
 10 in which the carrier is a soap.

12. A method according to claim 9 sub-
 stantially as hereinbefore described with
 reference to any of Examples 1 to 11.

13. A method of making a sponge accord-
 ing to claim 2 comprising mixing a soap and/
 or a detergent and a hot mass of abrasive
 scouring particles with a material capable of
 foaming to form a polyurethane foam and
 allowing the mixture to expand freely and to
 cure to form a resilient polyurethane foam
 having closed cells within which is the soap
 and/or detergent and scouring particles.

14. A method according to claim 13 in
 which the abrasive particles have a tempera-
 ture of from 65 to 125°C.

15. A method according to claim 13 or
 claim 14 in which the weight ratio of the
 abrasive particles to the foam forming
 material is from 4 to 6:1.

16. A method according to any of claims
 13 to 15 in which the foam forming material
 is the reaction product of a aryl diisocyanate
 and a polyether.

17. A method according to claim 16 in
 which the foam forming material is the re-
 action product of tolylene diisocyanate and
 polypropylene glycol.

18. A method according to claim 16 or
 claim 17 in which an alkali metal or
 ammonium salt of alginic acid is added to
 the mixture as a catalyst.

19. A method according to claim 13 substantially as hereinbefore described with reference to any of Examples 12, 13, 14 and 15. by a method according to any of claims 13 to 19. 10

- 5 20. A sponge according to claim 1 made by a method according to any of claims 9 to 12.
21. A sponge according to claim 2 made

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